

Conductivity of hydrogen halides in anhydrous acetic and propionic acids. M. HLASKO and E. MICHALEK (Recs. Chem., 1938, 19, 220-227) - The conductivity (κ) of HCl in anhyd. AcOH is $<$ of HBr; that of HI cannot be determined, owing to decompr. The κ of HCl in anhyd. $\text{CH}_3\text{CO}_2\text{H}$ is zero, and of HBr $<$ HI. In AcOH max. κ is obtained with $n\text{-HCl}$ or $1.4n\text{-HBr}$, and min. κ with $0.3n\text{-HCl}$ or $0.025n\text{-HBr}$; this is in disagreement with the Walden formula, according to which the concn. at which min. κ is obtained depends only on the ϵ of the solvent.

R. T.

APPROVED FOR RELEASE: 03/13/2001

CIA-RDP86-00513R001033810018-6"

Poland/Analytical Chemistry - Analysis of Inorganic Substances, G-2

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 1259

Author: Michalski, E., and Zuk-Kunaszewska, M.

Institution: None

Title: Electrometric Determination of Iodides by the Polarization of One Electrode

Original
Periodical: Tr. Note: This seems to be a book but is not marked by the letter K; publication data are Lodz. LTN, 1944, 18 pages

Abstract: The titration is carried out with an apparatus consisting of 2 vessels, one of which contains KI solution and the other, a saturated solution of $Hg_2(NO_3)_2$. The vessels are connected by an electrolytic bridge filled with KNO_3 solution. Two Pt electrodes are immersed in the solutions and connected to a galvanometer which is switched on during the titration only for short intervals for the purpose of observing the deflection. The electrode immersed in the KI solution constitutes the anode and is depolarized during titration. After the attainment of

Card 1/2

Poland/Analytical Chemistry - Analysis of Inorganic Substances, G-2

Abst Journals: Referat Chem. Kemiya Nauk., 1962; 12(2)

Abstract: Equilibrium at a sharp increase in the concentration of I^- ions takes place; this causes polarization of the anode and interrupts the current. Near the end of the titration the galvanometer can be switched on continually until the deflection is approaching zero. The mean error during the determination of 1/10, 1/50, 1/100 and 1/250 N solutions of $\text{K}_2\text{Cr}_2\text{O}_7$ is $\pm 0.05\%$; in the presence of chloride the error is $\pm 0.2\%$ and in the presence of bromide $\sim 1\%$.

Card 2/2

Michalski, E.

v. 407. Electrochemical determination of iodides based on the reduction of iodine by iodide (L. M. Tamm, V. V. Kabanov, and M. V. Slobodcikova (1947). Zhur. Nauk., Section 777, No. 1, p. 11 pp.).—A solution of an iodide to be titrated is connected by a bridge of KNO_3 with a 1M AgNO_3 soln. Immersed in each soln. are platinum electrodes connected through a galvanometer. A small current is registered which is due to the reaction $2I^- + I_2 \rightarrow 2I$. As the iodide soln. is titrated with AgNO_3 the iodide concn. decreases because of the formation of AgI , and the current drops. At the equivalence point a sudden fall in the current of iodine produces polarization, and the current stops. Iodide solutions of 0.004 to 0.1 N can be determined with a mean error of 0.05 per cent. Errors of 0.2 and 1 per cent., respectively, are obtained in the presence of chlorides and bromides. Chem. Abstr.

Sym ①
fch

MICHALSKI, Eugeniusz (Warszawa, ul. Bialobrzeska 17 * 33)

Visceral lupus erythematosus. Polski tygod. lek. 9 no.42:1362-
1365 18 Oct 54.

1. Z Oddzialu Chorob Wewnetrznych I.D.S.K.L.; kierownik: doc.
W.Hartwig, w Instytucie Gruslicki dyrektor; prof. J.Misiewicz.
(LUPUS ERYTHEMATOSUS,
visceral)

MICHAŁ SKI EDITIONS

POLAND/Analysis of Inorganic Substances

G-2

Abs Jour: Ref Zhur-Nauk, no 6, 1957, 1953

Author : Eugeniusz Miełalski, W. Filipczuk
Inst : Lódz University

Title : Electrometric Determination of Salts of Monovalent Mercury by Method of Polarizing Line of Electrodes.

Orig Pub: Zesz. Nauk. Univ. Łódzkiego. Matemat. Przyrodn., 1955, No 1, 135 - 143.

Abstract: The salts of $Hg(1+)$ are determined by the method of reversed titration of a known quantity of KI by the analysed solution of the $Hg(1+)$ salt. The titration end is estimated by the disappearance of the current in the circuit caused by the

Card 1/3

- 36 -

POLAND/Analysis of Inorganic Substances

G-2

Abs Jour: Ref Zhur-Khimiya, No 6, 19553

polarization of the indicator electrode (IE) in consequence of the elimination of the depolarizing ions I^- . The system consisted of two half-cells: IE and the comparison electrode (CE) connected with an electrolytic switch with a saturated solution of KNO_3 and of an galvanometer, sensitivity 1.9×10^{-8} a. IE and CE were made of Pt wire 0.5 mm in diameter and about 3 mm long. IE was submerged in the solution of KI, and CE was submerged in the solution of $Hg_2(NO_3)_2$, the concentration of which did not influence the determination result. The above system does not need any additional current source. The average errors of determination were: at 0.1 n. solution of

Card 2/3

- 37 -

Poland/ Analytical Chemistry - Analysis of Inorganic Substances

7-2

Abs Jour : Referat Zhur - Khimiya, No 3, 1957, 8459

Author : Michalski, E. and Jedrzejewski, W.

Inst : Lodz University

Title : The Electrometric Determination of Salts of Univalent Thallium
by the Polarization of the Indicator Electrode

Orig Pub : Zesz. nauk. Univ. Lodzkiego, ser. 2, 1955, No 1, 127-131 (in
Polish with summaries in English and Russian)

Abstract : The determination of salts of Tl^+ have been carried out by titrating a known amount of KI with the solution to be analyzed. The end point of the titration was determined by the return of the galvanometer needle to the zero position, caused by the polarization of the indicator electrode (IE) at the equivalence point. The system consists of 2 half-cells, the IE and the reference electrode, connected by a salt bridge filled with a saturated KNO_3 solution and of a mirror galvanometer with a sensitivity of $1.0 \pm 0.5 \times 10^{-8}$ ampc/division. The IE is prepared from Pt-wire having a diameter of 0.5 mm and a length of 4 mm, the reference electrode may be prepared either from Pt wire or from a Pt sheet with a total

Card 1/2

-29-

Roland / Analytical Chemistry - Analysis of Inorganic Substances

7-2

Abs Jour : Referat Zhur - Khimiya, No 7, 1957, 3459

surface of $\sim 0.3 \text{ cm}^2$ (in the first case, the reference electrode is dipped into a 0.02 N KI solution to which 1% alcoholic I₂ solution is added with constant stirring, and in the second case, into a saturated TlI solution). In the first case the error in the determination of solutions of concentration 0.1-0.05 N is from -0.0 to -1.2%, and in the second case, from 0.3 to 0.6%. When more dilute solutions are used in the titration greater errors are obtained. The presence of secondary electrolytes affects the results from the determinations. The advantages of the method consist in the simplicity of the equipment in comparison to the potentiometric method used up to the present time.

Card 2/2

- 30 -

MICHALSKI, E.

MICHALSKI, E. Definition by the coulometric method in chemical analysis. p. 492.

Vol. 9, no. 10, Oct. 1955

WIADOMOSCI CHEMICZNE

SCIENCE

Poland

So: East European Accession, Vol. 6, No. 5, May 1957

M. Chaliski Eugeniusz

After the decomposition of silver, the remaining hydroxide was decomposed by heating at 200°C. The residue was dissolved in dilute HNO₃ and the solution was titrated with standard NaOH. The titration was carried out in the presence of excess Cr³⁺, Cu²⁺ and Fe²⁺ by titration with KI solution. The titration results were expressed in terms of silver. The end point was indicated either graphically or from potentiometric titrations in a closed circuit. At a constant current of 0.5 A, the titration yield of Cr and Cu, the error was less than 0.5%.

pm 10

MICHALSKI, EUGENIUSZ

N,N'-Dipropyl-, N,N'-diphenyl-, N,N'-diethyl- and N,N'-diallylbiacridinium nitrate as chemiluminescent indicators.

Eugeniusz Michalski and Maria Turowska (Ural, 1/4)

Received June 10, 1987 (1986) English summary).

N,N'-Dipropyl- (I), N,N'-Diphenyl- (II), N,N'-diethyl- (III), and N,N'-diallylbiacridinium nitrate (IV) were investigated as acidobasic chemiluminescent indicators for the titration of strong acids by strong bases and of weak acids by strong bases. The catalytic influence of MeOH, EtOH, PrOH, and iso-BuOH on the titration results was also examined. I, II, III, and IV can be used as indicators for titration of strong acids by strong bases. In the presence of alcohols, the titration end point appeared at lower pH values. Good results were obtained with II and IV by adding iso-BuOH. Titration of weak acids by strong bases with I, II, III, and IV gave good results in the absence of alcohols. Titration of strong bases by weak acids was possible only in the presence of iso-BuOH.

Z. Kuryska

POLAND / Analytical Chemistry. Analysis of Inorganic E-2
Substances.

Abs Jour: Ref Zhur-Khimiya, No 1, 1959, 969.

Author : Michalski, E., Ruskul, W.

Inst : Not given.

Title : The Amperometric Titration of Bismuth Without
Using External Current.

Orig Pub: Chem analit., 1957, 2, No 3, 284-285.

Abstract: A description is given on a method which is based on a previous precipitation of Bi in the form BiOI, the precipitate obtained is dissolved in HCl and the iodine is then titrated amperometrically with silver nitrate solution, without using any external current. Potassium iodide is added (in a small excess) to the solution being analyzed, the mixture is diluted with hot water and a solution of sodium acetate is added. After the pre-

Card 1/3

16

POLAND / Analytical Chemistry. Analysis of Inorganic E-2
Substances.

Abs Jour: Ref Zhur-Khimiya, No 1, 1959, 969.

Abstract: cipitate which formed had settled, the solution is filtered by suction through a sintered glass funnel and the precipitate of BiOI is washed twice with a small amount of water and dissolved in 18-40 ml of 3% HCl (depending on the amount of precipitate). The solution obtained is diluted with water to approximately 150 ml and while stirring vigorously is titrated amperometrically with 0.01-0.1 N solution of silver nitrate. The end point is determined graphically from a curve which expresses the relationship between current strength and the volume of the silver nitrate solution added, or directly from the zero location of the galvanometer indicator. The amperometric titration without external voltage is conducted by using an indicating Pt electrode which is placed into the

Card 2/3

MICHALSKI, E.

Preparation of pure crystalline sodium hydrosulfide.
Eugeniusz Michalski, Ryszard Grochowski, and Zbigniew
Cieplik (Wrocław, Poland). Zeszyty Nauk. UAM,
ser. 77, Nauki Mat.-Przyrod. No. 3, 125-32 (1957) (English
and Russian summaries).—Ca(OH)₂ (120 g.) of 70% purity
was added to a suspension of 1 kg. Na₂S of 61% purity in 3
kg. H₂O. The mix. at 95° was satd. with H₂S flowing at
16 l./hr. and was cooled to 50° when the Na₂S was dissolved.
H₂S addn. was stopped when the pH became nearly const.
Pale yellow NaHS·3H₂O contg. 50.8% NaHS crystd. at 27°.
J. Stecki

COUNTRY : Poland n-1
CATEGORY :

ART. JOUR. : RZKhim., No. 1959, No. 9C10

AUTHOR : Micielski, B.

J. T. :
TITLE : Amperometric Titration without Application
of External Voltage

ORIG. PUB. : Chem. analit., 1958, 3, No 3-4, 423-430

ABSTRACT : It is shown that there is considerable
similarity between amperometric and potentiometric titration.
In particular, amperometric titration without application
of external voltage is analogous to classical potentiometric
titration: in the 1st method is used one indicator electrode
which can be, depending upon choice of comparison electrode,
the cathode or the anode; while the titration reagent plays
the role of depolarizer (polarizer) of indicator electrode.
The theory of amperometric titration without application
of external voltage, is described. At the author's laboratory
methods have been developed for determination of Fe^{2+} , Mn^{2+} ,
 Cr^{2+} , Hg_2^{2+} , Bi^{3+} , Ti^{4+} , Cl^{2-} , and also of oxalic, tartaric,
and citric acid. -- V. Mirkin.

CARD:

75

APPROVED FOR RELEASE: 03/13/2001

CIA-RDP86-00513R001033810018-6"

COUNTRY : Poland
CATEGORY :
JSS. JOUR. : RZhKhim., no. 1959, No. 6100
AUTHOR : Michalski, E.; Stojer, W.
INFO. :
TITLE : Amperometric Titration of Tin(IV) with I₂
Application of External Voltage
ORIG. PUB. : Chem. analit., 1959, 3, No 3-4, 441-444

ABSTRACT : Description of amperometric titration of Tl⁺ with a solution of KI, in a medium of 20% C₂H₅OH, without application of external voltage, using a stationary and a rotating Pt-electrode. As the comparison electrode is used a calomel electrode in which saturated KCl-solution is replaced by a solution of KNC₃; the potential of such an electrode is close the potential of indicator Pt-electrode at equivalence point. Best results were obtained on using a rotating Pt-electrode. By the described method, up to 0.6 mg Tl⁺ can be determined with an error of 0.1%.

CARD:

b-2

COUNTRY : Poland
CATEGORY : Analytical Chemistry--General
ABS. JOUR. : RZKhim., no. 22 1959, no. 78256
AUTHOR : Michalski, E. and Tirowska, M.
TITLE : Not given
: Derivatives of diacridine as Chemiluminescent
Indicators.
ORIG. PUB. : Chem Analit., 3, no 3-4, 599-607 (1958)
ABSTRACT : The feasibility of the application of the nitrates
of N,N'-dipropyl- (I), N,N'-ditolyl- (II), N,N'-
diphenyl- (III), and N,N-disallyldiacridine (IV)
as chemiluminescent indicators (CI) in the titra-
tion of strong acids with strong bases has been
investigated. 0.01 N, 0.1 N, and 0.5 N solutions
of HCl and NaOH were used in the titrations. To
the solutions to be titrated are added 5 ml of a
0.04% solution of CI and 5 ml of 3% H_2O_2 ; the
resulting solution is titrated in the dark (mag-
netic stirring) with CO_2 -free NaOH. The endpoint

JAD: 17

COUNTRY : Poland
CATEGORY :
ART. JCUP. : RZKHM., No. 22 1959, No. 76-56
AUTHOR :
INST. :
TITLE :
S. IN. PUP. :

ABSTRACT : of the titration is determined by the appearance of yellow-green chemiluminescence throughout the solution on the addition of 1 drop of NaOH; in the titration of NaOH solutions with HCl solutions the endpoint is determined by the disappearance of the yellow-green chemiluminescence. Potentiometric measurements have shown that the indicator color change takes place at pH 6.0 for I, 7.7 for II, 9.2 for III, and 10.1 for IV. In order to determine the accuracy of the titrations, duplicate titrations were made using bromthymol blue

CARD: 24

63

MICHALSKI, E. ; CZARNICKI, K.

Amperometric determination of some organic acids without additional voltage from outside. p. 83.

CHEMIA ANALITYCZNA. Warszawa, Poland. No. 8, August 1959.

Monthly List of East European Accessions (EEAI) LC, Vol. 8, No. 11
November 1959.

Uncl.

MICHALSKI, Eugeniusz; TUROWSKA, Maria

Analytical application of chemiluminescent diacridine derivatives.
I. Identification of some aliphatic alcohols. II. Determination of
methanol and ethanol in their mixture. Chem anal 5 no.4:625-636
'60. (EEAI 10:9)

1. Department of Inorganic Chemistry, University, Lodz.

(Biacridine) (Luminescence) (Aliphatic compounds)
(Alcohols) (Methanol) (Ethyl alcohol)

MICHALSKI, Eugeniusz, prof. dr.

Amperometric analysis and its development in recent years. *Wiad chem* 14 no.7:411-423 J1 '60.

1. Kierownik Katedra Chemii Nieorganicznej, Uniwersytet, Lodz.

MICHALSKI, Eugeniusz; WALEWSKI, Ludwik

Catalytic microdetermination of phosphate by means of amperometry.
(EEAI 10:9)
Chem anal 6 no.2:273 '61.

1. Department of Inorganic Chemistry, University, Lodz.
(Phosphates) (Conductometric analysis)

MICHALSKI, Eugeniusz; WTORKOWSKA, Albina

Catalytic ultramicrodetermination of thiocyanide on the basis of
amperometric measurements. Chem anal 6 no.3: 365-375 '61.

1. Department of Inorganic Chemistry, University, Lodz.

MICHALSKI, Eugeniusz; PAWLUK, Natalia

Amperometric Red-ox titrations without external voltage. II.
Titration of reversible systems by reversible titrants.
Chem anal 6 no.6:943-948 '61.

1. Department of Inorganic Chemistry, University, Lodz.

BIALECKI, S.; BOJKO, M.; JOZEFACIUK, D.; LESZEK, H.; MICHALSKI, E.;
RUSZCZYNSKA, J.; SARNECKA, D.; WOJCIECHOWSKI, J.

Causes of delayed union and pseudarthrosis of the long bone. Chir.
narz. ruchu ortop. polska 26 no.5:597-604 '61.

1. Z Kliniki Ortopedycznej AM w Warszawie Kierownik: prof. dr.
A.Gruca.
(FRACTURES UNUNITED etiol) (PSEUDAETHROSIS etiol)

MICHALSKI, Eugeniusz; WTORKOWSKA, Albina

Catalytic determination of trace amounts of thiosulfate ions
by amperometric measurements. Chem anal 7 no.4:783-790
'62.

1. Department of Inorganic Chemistry, University, Lodz.

MICHALSKI, Eugeniusz; GELOWA, Helena

Catalytic determination of microgram amounts of germanium
on the basis of amperometric measurements. Chem anal 8
no.4:643 '63.

1. Department of Inorganic Chemistry, University, Lodz.

MICHALSKI, Eugeniusz

ASKANAS, Zdzislaw; Czerwinska, Stanislawa; LISZEWSKA, Danuta;
MICHALSKI, Eugeniusz; RUDNICKI, Stanislaw; RYWIK, Stefan;
SLIDZIEWSKI, Konstanty

A method for the selection of a representative sample for the
investigation of the level of arterial pressure in large popu-
lation groups. Pol. tyg. lek. 20 no.23:830-834 7 Je '65.

1. Z Centralnej Przychodni Chorob Ukladu Krazenia w Warszawie
(Kierownik: prof. dr. med. Zdzislaw Askanas).

KIRSCHNER, Henryk; NIKI-LSKI, Wald

The value of determining the physical capacity based on a
brief effort test. Med. prace 16 no.2:110-112 '65

Z Zeszytu Przegl. Med. i Sanit. Nr 10 1965

MICHALSKI, Henryk; SERWINSKI, Mieczyslaw

Determination of the mass-transfer coefficient in a distillation
wotted-wall column. Roczn techn chem zyw 8:87-97 '61.

1. Department of Chemical Engineering, Institute of Technology,
Lodz.

MICHALSKI, Ireneusz

Taxonomic and populationistic trends in modern anthropology; some
remarks in connection with Tadeusz Bielicki's article: "The Anthropo-
logical Controversy on the Concept of Race," Kosmos biol 12 no.1:
51-78 '63.

MICHALSKI, Franciszek

The program of complex wood treatment. Pt.3. (To be contd.) Przem
drzew 12 no.12:1-3 '61.

(Wood)

MICHALSKI, Franciszek

On the programme of complex wood treatment. Pt. 4. Przem drzew 13
no. 1:4-7 Ja '62.

COUNTRY : POLAND H
CATEGORY : Chemical Technology. Chemical Products and
Their Applications. Chemical Engineering
AB5. JOUR. : RZKhim., No. 3 1959, No. 82521
: Tacholski, E.; Strumillo, G.; Szapiro, S.
: -
TITLE : Determination Method of Packing Height in
Rectifying Columns
CRIP. PUB. : Zesz. nauk. Politechn. lodzkiej, 1957, No 16,
3-14
ABSTRACT : A method for determination packing height is
proposed which is based on the results of
experiments conducted by the authors on a
laboratory installation and suitable for cal-
culations of commercial rectifying columns.
A satisfactory correlation of data is estab-
lished when employing factors obtained by the
proposed method as well as data found by the
others. A satisfactory correlation exists
also with data obtained by the authors in
their experiments with different packed colu-
mns.
CARD: 1/1

ACC NR: -A1302894-

AM7002488

Michalski, Henryk

Monograph

PO/

Territorial defense strategy and tactics (Strategia i taktyka obrony terytorium kraju) [Warsaw; Wyd-wo MON] 1965. 451 p. illus., bibliog. Errata slip inserted. 1,500 copies printed. Series note: Biblioteka Polskiej mysli wojskowej.

TOPIC TAGS: civil defense, air defense system, military operation, ground force tactic

PURPOSE AND COVERAGE: This book, published by the publishing house of the Ministry of National Defense, Warsaw, is intended for the general reader. Based on Western, Polish, and Soviet sources, it presents a general survey of the modern territorial defense system of a country, with emphasis laid on the defensive needs of Poland. Particular attention is given to the role of civilians in territorial defense. The text includes 18 diagrams and other tables and illustrative material.

TABLE OF CONTENTS [abridged by the abstracter]:

Some history up to 1945 -- 13

Ominous implications of new weapons -- 43

Card 1/2

ACC NR: AM7002488

~~AN5028974~~

Territorial defense considered within the defense system of a country -- 77

Functions of territorial defense -- 101

A uniform or functional system -- 133

Prospects for modern aerial defense -- 188

Land-based territorial defense system -- 240

Civil defense as a part of a territorial defense system -- 284

Preparing the rear area to repulse aggression -- 328

First days of war -- 371

Looking into the future -- 424

SUB CODE: 15/ SUBM DATE: 13Nov64 / SOV REP: 006/ OTH REF: 165/

Card 2/2

MICHALSKI, I,

GEOGRAPHY & GEOLOGY

PERIODICAL: CZŁOWIEK W CZASIE I PRZESTRZENI. Vol 4, no. 4, 1958

MICHALSKI, I. Anthropological types in Egypt, p. 192

Monthly List of East European Accesories (EAA) LC. Vol 6, no. 4
May 1959, Unclass.

AGRAHAM, I.

TELETYPE

Periodicals: TELETYPE, TELETYPE, TELETYPE, TELETYPE

AGRAHAM, I. From the State and the internal intelligence services
foreign nations; other foreign information.

Monthly; it is sent by teletype messages (TELETYPE), TELETYPE, TELETYPE.

MUKHABERSKIY, V.A. [M: mukhaber] [redacted]

Newspaperman, 30 years old, married, 5'7", 165 lbs.
(Candidate, Second class).
Vyschaya shkola po vospitaniyu i obrazovaniyu, zatezhka
zauchchity lezha, "Zvezda", 1964.

Michalski, J.

POLAND / General and Special Zoology. Insects.
Systematics and Faunistics.

P

Abs Jour: Roc Zhur-Biol., No 21, 1958, 95405.

Author : Michalski, J.

Inst : Not given.

Title : A List of Bark Beetles of the Kłodzko Region.

Org Pub: Polskie pismo ontomol., 1956 (1957), 26, No 1-26,
161-170.

Abstract: A list of 31 species of bark beetles from south-
west Poland, a map of distribution and a diagram
of the vertical dissemination of the species.

Card 1/1

8

Author : Michalski, J.

Inst : -

MICHALKSI, Jack
SZMIDT, A.

Observations on some methods of fighting Blastophaga. p. 55

SYLWAN. (Wydział Nauk Rolniczych i Lesnych Polskiej Akademii Nauk i Polskie
Towarzystwo Lasek) Warszawa, Poland
Vol. 101, no. 7, July 1957

Monthly List of East European Accessions Index (EEAI), LC, Vol. 8, no. 6, June 1959
Uncl.

MICHALSKI, Jacek

Natural enemies of Scolytus (Scolytochelus) ensifer Eichh.
(Coleoptera, Scolytidae). Prace nauk roln i lesn 13 no.1:15-49 '62.

1. Katedra Ochrony Lasu, Wyższa Szkoła Rolnicza, Poznań.

BALAZY, Stanislaw; MICHALSKI, Jacek

The parasitic Hymenoptera of the (Coleoptera, Scolytidae)
occurring in Poland. Prace nauk roln i leśn 13 no.1:71-141
'62.

MICHAEL J. BACK

Biology of the Arctic Fox, Vulpes lagopus, in the Svalbard
Islands - back number 31-72 1-1

Department of Forest Protection, University of Oregon,
Eugene

SA

POLAROID K15

10

Cholic acids. J. Hradáček and J. Michálek
Frakthe /Büren/ 62, 120 561900, České Budějovice,
extended the side chain of 3-hydroxy-7-ketocholic acid
and by the prep. of the acetoxy, diacetox, triacetox,
chloro-, and amide compds. The syntheses were verified by
elemental analyses

1982

MICHALSKI JAN

Organic phosphorus compounds. I. Addition of di-
ethyl hydrogen phosphonate to ethylenic derivatives.
Boleslaw Kochan and Jan Michalski (Inst. Technol. Lek.,
Poland). Roczniki Chemii 23, 886 (1951) [English sum-
mary]; cf. C.A. 46, 8867. A new method for the synthesis
of phosphinic acids is described; it is based on the aldol
reaction of dialkyl α -phosphonates to unsatd. compds.
contg. activating groups (CO , CO_2R , CN) in α -position to
the ethylenic bond. To 19.4 g. $\text{HPO}(\text{OEt})_2$ (I) in 20 ml.
 C_6H_6 in a flask with stirrer, dropping funnel, thermometer,
and CaCl_2 tube, was added 0.15 g. Na, the flask cooled
to 10° , 13.7 g. $\text{MeCH}_2\text{CHCO}_2\text{Me}$ in 25 ml. C_6H_6 added
dropwise at $15-20^\circ$, the mixt. let stand 24 hrs., the brown
product dissolved in 100 ml. C_6H_6 , the soln. washed with a
NaCl soln., in 0.1N HCl, and then NaCl in water, the C_6H_6
layer dried with MgSO_4 and dark brown product distd. in
vacuo, giving 23.3 g. (82%) $\text{Me}_2\text{C}=\text{CHPO}(\text{OEt})_2$ (II), m.p. $83-4^\circ$. Hydrolysis of 5 g. II with 25 ml. 20%
HCl gave 2-phosphonobutyric acid (III), colorless needles
from glacial AcOH, m. $110-61^\circ$, sol. in H_2O , alc., and
 Me_2CO , insol. in ether, C_6H_6 , and ligroine. II was also ob-
tained from $\text{MeCH}_2\text{CH}_2\text{CO}_2\text{Et}$ (IV); a suspension of
1.03 g. Na in 50 ml. boiling PhMe in the app., described
above, cooled to 70° , 0 g. I added dropwise at a temp. up to
 80° , the flask warmed in a water bath 2 hrs., 0 g. IV then
added dropwise at $60-70^\circ$, the flask warmed another 2 hrs.,
the cooled product washed with稀的 NaCl, and the Ph-
Me layer dried with MgSO_4 and distd. in vacuo gave 8.3
g. (62%) II, b. $70-80^\circ/0.001$ mm., n_D²⁰ 1.4381. Na (0.15
g.) in a mixt. of 19.4 g. I and 20 ml. C_6H_6 treated dropwise
with 17.2 g. $\text{CH}_2=\text{CHCO}_2\text{Me}$ at 10° (exothermic reaction)
with the temp. kept at $20-5^\circ$, and the product, $\text{Me}_2\text{C}=\text{CHPO}(\text{OEt})_2$
(V), distd. under 0.001 mm.
Hg gave 2 fractions: to 78° (3.0 g.), $78-80^\circ$ (0.6 g.), $90-$
 120° (7.0 g.), n_D²⁰ 1.4393, 1.4381, 1.4402, resp.; and 3 frac-

tions upon hydrolysis with 20% HCl gave cryst. $(\text{HO})_2\text{P}(\text{OEt})_2$
(VI). $\text{PhCH}_2\text{CHCO}_2\text{Et}$ (26.4 g.) added
dropwise at $15-20^\circ$ to 19.4 g. I in 20 ml. C_6H_6 , contg. 0.15 g.
Na, gave 1.5 g. (40%) $\text{Et}_2\text{C}=\text{CHPO}(\text{OEt})_2$ (VII), $\text{m.p. } 123^\circ$. Hydrolysis of 5.0 g. VII yielded
2.0 g. 2-phosphono-3-phenylpropionic acid (VIII), colorless
needles from glacial AcOH, m. $189-202^\circ$. Similarly, 19.4 g.
I in 20 ml. C_6H_6 and 0.15 g. Na with 21.7 g. PhCH_2CHAc in
15 ml. C_6H_6 at $15-20^\circ$ gave 23 g. (68 g.) $\text{I}-\text{phenyl-1-(diethyl-}$
 $\text{phosphono)-1-butanoic}$ (IX), m.p. 117°. Hydrolysis of 10 g.
IX with 30 ml. 20% HCl in 10 hrs. gave 8.1 g. (90%) crude
keto acid (X), crystn. of which failed. X (0.1 g.) in 1 ml.
 MeOH treated with Brady reagent [$2,4-(\text{O}_2\text{N})_2\text{C}_6\text{H}_3-\text{NH}_2$; cf. C.A. 25, 2310] gave the 2,4-dinitrophenyl-
hydrazone (XI), yellow needles, from acq. MeOH , m. $103-4^\circ$.
XI (6.8 g.) in 50 ml. H_2O added dropwise to 6.6 g. NaOH,
12 g. Br, and 200 ml. H_2O , the mixt. heated 1 hr. at 70° ,
acidified with 20 g. 30% HCl, 3 g. Na_2SO_4 added, the soln.
evapd., the residue dried, extd. with 300 ml. EtOH , the
ext. evapd., and the cryst. residue recrystd. from glacial
 AcOH gave VIII, m. $189-201^\circ$. II (25.2 g.) in 60 ml.
 C_6H_6 and 0.2 g. Na treated dropwise to 6.6 g. $\text{C}_6\text{H}_5-\text{CH}_2\text{CN}$ at $20-3^\circ$ (exothermic reaction) gave 27 g. (84%)
 $\text{di-Bu}(\text{2-cyanoethyl})\text{phosphonato}$ (XII), m. $143-4^\circ/0.8$ mm.
XII (5.0 g.) hydrolyzed 10 hrs. with 23 ml. 20% HCl,
evapd., and the residue dried over KOH , extd. with 100
ml. EtOH , and recrystd. from H_2O yielded 2.7 g.
(87%) 3-phosphonopropionic acid, m. $107-8^\circ$.

Gene A. Worley

MICHALSKI, J.

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~~Received May 10, 1954. From and by J. Michalski, J. Michalski, et al. (1951). Roczniki Chem. 25, 814-819 (1951) (English summary).~~
Tetraalkyl thiopyrophosphates of the thioanhydride type were prep'd.: (A) by condensation of the corresponding dialkyl chlorophosphonates with salts of dialkyl thiophosphoric acids according to $(RO)_2P(O)SNa + C(O)P(OR)_2 \rightarrow (RO)_2P(O)S(O)P(OR)_2 + NaCl$, and (B) by action of H₂S on dialkyl chlorophosphonates in the presence of a tertiary base (e.g. C₆H₅N) according to $2(RO)_2P(O)Cl + H_2S + 2C_6H_5N \rightarrow (RO)_2P(O)S(O)P(OR)_2 + 2C_6H_5NHCl$. The following thiopyrophosphates were prep'd.: *tetra-Bu*, *b.p.* 120-2°, (74%), *tetra-iBu*, *b.p.* 82-4° (66%), *tetra-Bu*, *b.p.* 113-14° (72%), and *tetra-iBu*, *b.p.* 90-8° (72%). G. A. W.

Michalski, J.

Addition of phosphonoacetic esters and their analogs to
α,β-unsaturated ethylenic derivatives. B. Fijner and J.
Michalski (Politechnika Krakow Chem. Organ., Krakow, Poland).
Zhurnal Russkogo Khimicheskogo Instituta, 26, 203-210 (1974) (English summary).—
Phosphonoacetic esters and their analogs are prepd. by the
addn. of $(RO)_2P(O)CPOHCO_2R$, and $(RO)_2R'P(O)CR'II$
 CO_2R in the presence of basic catalysts to unsatd. esters and
nitriles. Thus were prepd. the following (compd., b.p./
mm, n_{D}^{20} , d_4° given): $EtO_2C(NCCH_2CH_3)CHPO(OEt)_2$,
112–17°/70.06, 1.1470, 1.1168; $EtO_2C(NCCH_2CH_3)CPO$
 $(OEt)_2$, 145–7°/0.02, 1.4380, 1.1361; $EtO_2CMeOCOCH_2$
 $Bu_2CPO(OEt)_2$, 117–19°/0.06, 1.4520, 1.0973; EtO_2C
 $(Bu)_2NCCCH_2CH_3CPO(OEt)_2$, 116–18°/0.035, 1.4512,
1.0681; $(EtO_2CCH_2CPOH)(EtO_2CCH_2CPO(OEt)_2)$, 138°/
0.03, 1.4979, 1.4907; $EtO_2CMeOCCH_2CH_3CPO$
 $(OEt)_2$, 134°/70.006, 1.5048. — R. L. Whittaker

MICHALSKI, J.

J. Simplified method for preparation of dialkyl chlorophosphonates.
B. Eizner and J. Michalski (*Recue. Chim.*, 1952, 26, 681-689)
The method described consists in treating 1.5 mol. of dry benzene
in an equal volume of a suitable alcohol with 0.5 mol. of PCl_3 (diluted
with 0.5 mol. of benzene) and 0.5 mol. SO_2Cl (diluted with 0.5 mol.
of benzene) at 8-11°. The gaudous reaction products, alkyl chloride
and the solvent, are distilled off at room temp., under reduced
pressure, and the dialkyl chlorophosphonate formed is purified by
vac. distillation. The reaction time is considerably shortened and
the yield increased by about 10% by using this method (~90%
yield for Et_2 , Pr_2 , Pr_2^t , Bu_2 , and Bu_2^t esters). A. STORER.

MICHALSKI, JAN

POL.

*Organosulfur compounds of sulfur and selenium. I.
Synthesis of tetraalkyl thiophosphates. Part 1. 2
Mr. Jan Michałski and Jan Węcławowski (Polish Tech.
Lad. Chem., Warsaw) (Chem. Z., 622-631, 1983) give
summary.—Tetraalkyl thiophosphates, $(RO)_4P(O)SP(O)R'$, may be prep'd. by: (1).—condensation of NaO_2 -diethylthiophosphate with dialkyl chlorophosphates or
(2).—action of H_2S on dialkyl chlorophosphates in the presence of tertiary amines. Toxicity and anticholinesterase
activity of the products were studied. Dialkyl chloro-
phosphates were prep'd. using the method described pre-
viously (cf. C.A. 49, 2306c). NaO_2 -diethylthiophosphate
were obtained by adding 0.25 mole powd. S in small por-
tions with stirring and outside cooling to a mixt. of 0.2
mole Na dissolved in 60 ml. dry ROH and 0.21 mole dialkyl
phosphate in 80 ml. dry H_2O . Stirring was continued after
all the S was added until the mixt. warmed up to room
temp. The excess S was filtered and the filtrate was evapd.
under reduced pressure at room temp. The cryst. product
was washed 3 times with H_2O and evapd. each time.
Di-Et phosphite gave 91% yield (based on Na). Crude (400)
 $P(O)SNa$ (I), m. 188° (m. 203° (from $CHCl_3-H_2O$).
Crude I was used in further syntheses. $(EtO)_4POCl$ (II),
(21.5 g.) (0.125 mole) added dropwise with vigorous stirring
to a remaining mixt. of 24 g. (0.125 mole) powd. dry I and
120 ml. anhyd. Et_2O , refluxed for 30 min., dild. with 100 ml.
 C_6H_6 , washed successively with: 100 ml. water, a few
drops pyridine, 50 ml. 1% HCl, 50 ml. water, 50 ml. 5%
 $NaHCO_3$, and 50 ml. water, dried with Na_2SO_4 and distd.
twice gave 20 g. (65%) $(EtO)_4P(O)SP(O)Et_4$ (III), b.p.
120-2 m. 185°, n_D²⁰ = 1.4400. Similarly, (MeO)
120-2 m. 185°, n_D²⁰ = 1.4400. Similarily, (MeO)*

BERNARD FISHER

Reaction (IV) and $(MeO)_2POCl$ gave 21% $(MeO)_2PO(OEt)_2$, colorless liquid, b.p. 122-125° (decomposed slightly), η_{D}^{20} 0.93 (b.p. at 100°), d_4^{20} = 1.2201, n_D^{20} = 1.4312. IV and II gave 50% $(MeO)_2PO(OEt)_2$ (VI), colorless liquid, b.p. 118°, d_4^{20} = 1.2545, n_D^{20} = 1.4103. I and $(BuO)_2POCl$ gave 87 g. crude product which in a mol. distn. (at 6.00 ml. min., condenser at 25 mm. from liquid surface, dist. at 5 drops/min.) gave the following fractions: (1).—6 g., temp. of liquid 50-55°, n_D^{20} = 1.4308; (2).—13.5 g., temp. of liquid 55°, n_D^{20} = 1.4471, 16.5% F [calcd. for $(BuO)_2PO(OEt)_2$] 17.1% F; (3).—27.5 g., temp. of liquid 55°, n_D^{20} = 1.4415, 14.5% F; (4).—4.5 g. (temp. of liquid 117°, n_D^{20} = 1.4340). I and $(PrO)_2POCl$ (VII) gave 77% $(PrO)_2PO(OEt)_2$, colorless liquid, b.p.m. 108.5°, d_4^{20} = 1.1847, n_D^{20} = 1.4428. II (34.5 g., 0.3 mole) was added dropwise with stirring at 10-15° to 70 ml. dry pyridine and a strong stream of H_2S was passed through the stirred and cooled mixt. for 90 min. The potd. $C_6H_5N\cdot HCl$ was filtered and washed twice with 75 ml. C_6H_6 . The combined filtrates were dried under reduced pressure and the residue taken up in 100 ml. C_6H_6 , washed successively with 50 ml. 2% HCl , 50 ml. water, 50 ml. 5% $NaHCO_3$, and 50 ml. water, dried with Na_2SO_4 , and dried twice gave 22 g. (74%) III, b.p. 55-6°. An 85% yield of III was obtained when N-methylmorpholine (1 ml. with C_6H_6) was used instead of pyridine. Similarly, VII and II in pyridine gave 87% $(PrO)_2PO(OEt)_2$ (VIII), colorless liquid, b.p. 55-62°, d_4^{20} = 1.1975, n_D^{20} = 1.4363; $(iso-PrO)_2POCl$, b.p. 55-60°, d_4^{20} = 1.1985, n_D^{20} = 1.4370; $(BuO)_2POCl$ gave 75% $(BuO)_2PO(OEt)_2$ (IX), yellow liquid, b.p. 112-14°, d_4^{20} = 1.076, n_D^{20} = 1.4517; $(so-BuO)_2POCl$ gave 72%

BERNARD FISZER

(*tert-butyl*) $P(OBu_2)_3$ (III), obtained from $Ph_3P + 2Bu_3OPOCl$, $M_n = 300$, $n_D^{20} = 1.4625$; (*MnO*) $POCl$ (below 6%) gave a viscous, colorless liquid, best in org. solvents, 1.0 g. in water. Et₂N (0.25 mole) added dropwise to 0.3 mole of Mn powder and 0.6 mole CCl_4 and treated with H_2 with stirring at 5-10° for 8 hrs. gave 60% III. All melting points are exco. Tetraalkyl thiophosphates are very insolubles. The following doses (in μ /kg. wt. of animal) were fatal to mice and rats when injected intraperitonealy: III, 0.000066; V and X, 0.000066; VI, 0.001; VII, 0.0016; IX and XI, 0.06. All compounds stopped cholinesterase activity in rat brain, III being the most active and suppressing parathion to effectiveness. J. R. Sosman

MICHALSKY, Jui

Preparation of 1,4-dimino-2-butene. E. Michalsky,
J. Hudlicky, and R. L. Hedges, University of Illinois, Urbana,
Illinois, and J. Org., 37, 1230-11 (1963).— $\text{H}_2\text{NCH}_2\text{CO}-$
 $\text{CH}=\text{CH}_2$ (II) was prep'd. by the following series of reac-
 tions : $\text{e-C}_6\text{H}_5\text{CO}_2\text{Na}$, NCI_2COCl , and CH_3N_3 gave 90% e-
 $\text{CH}(\text{CO})_2\text{NCH}_2\text{COCH}_3$, m. 167-8° (decomp.), (from
 $\text{e-C}_6\text{H}_5\text{CO}_2\text{Na}$). This was transferred in 65% yield to e-
 $\text{C}_6\text{H}_5\text{CO}_2\text{Na}$, m. 71-6° (from Et₂O). This
was hydrolyzed with 20 hrs. at 65° with 4M HBr
(4:1Et₂O) to give $\text{e-C}_6\text{H}_5\text{CO}_2\text{NH}_2$, m. 148-9°
(from $\text{C}_6\text{H}_5\text{CO}_2\text{Na}$), treated with SOCl_2 , and then with
 CH_3N_3 yielded 75% $\text{e-C}_6\text{H}_5\text{CH}(\text{CO})_2\text{NCH}_2\text{COCH}_3$ (III),
m. 123° (from Et₂O). Treatment of III with HCl in Et₂O
gave 82.7% yield of $\text{e-C}_6\text{H}_5\text{CH}(\text{CO})_2\text{NH}_2$; this
heated with $\text{e-C}_6\text{H}_5\text{CO}_2\text{Na}$ 6 hrs. on the steam bath
yielded 83% of 1,4-dimino-2-butene, m. 249-0°,
which reduced 30 hrs. with 37% HCl in AcOH (1:1) gave
78% I, m. 220-1° (decomp.). M. Hudlicky.

[Handwritten signature]

NICHOLSKI, JAN

POL.

Synthesis of organophosphorus compounds based on phosphonocarboxylic ester and its analogs. Addition of phosphonocarboxylic ester, alkylated phosphonocarboxylic esters, and phosphonooacetic nitrile to α,β -unsaturated esters and nitriles. Bernard HEAT and Jan NICHOLSKI (Higher Polytechnic School, Lublin, Poland). *J. Polym. Sci.*, 26, 185-97 (1954) (English summary). — $(BzO)_2P(OCH_2CO_2Et)$ (I), $(Et_2O)_2P(OCH_2CN)$ (II), and alkylated I (III) in the presence of alk. catalyst undergo Michael condensation with α,β -unsatd. esters and nitriles at 20-50° in CaH_2 or PhMe (less satisfactory results are obtained in aq. soln.). III are less reactive than I or II while the order of decreasing reactivity of α,β -unsatd. compounds (IV) is: acrylates > crotonates, methacrylates > $PhCH=CHCO_2Et$ (V). Condensation of active reagents (e.g., I with $CH_2=CHCN$ (VI) or $ClF_3 \cdot CHCO_2Me$ (VII)) is exothermic, requires small量 of catalyst, and yields a mixt. of mono- and disubstituted derivs. Condensation of a reactive P compd. with less reactive IV requires heating, more catalyst and can be stopped at the first stage, while the poorly reactive compds. do not condense even under drastic conditions due to steric hindrance. A mechanism of condensation is given. To 23 g. Na finely dispersed in 400 ml. dry xylene was added with cooling and stirring (Hg-sealed stirrer) 133 g. $HPO(OEt)_2$ (VIII), followed by 150 g. $ClCH_2CO_2Et$ (IX), the mixt. heated 6 hrs. on the bath at 60°, NaCl centrifuged off, the xylene removed, and the residue dried.

10 hrs. through a short column, yielding 102 g. $(\text{EtO}_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et})$ (X), m.p. 147-0°, n_D²⁰ 1.4392 (all b.ps. and m.ps. unrec.). X was added with stirring (46°C) to a mix. of 13 g. S in 20 ml. xylene (exothermic reaction). The heat. cooled and to it was added 47 g. S. After the ppt. filtered off, the filtrate washed with 1% HCl, H₂O, 5% NaHCO₃, and H₂O; the xylene layer dried over CaSO_4 , the xylene removed, and the residue dried, in above, yielding 92 g. $(\text{EtO}_2\text{P}(\text{O})\text{CH}_2\text{BuCO}_2\text{Et}$) (XI), b.p. 121-2°, n_D²⁰ 1.4380. $(\text{EtO}_2\text{P}(\text{O})\text{CH}_2\text{BuCO}_2\text{Et}$) (XI) and 23 g. $\text{BuCH}_2\text{BrCO}_2\text{Et}$ were refluxed 4 hrs. on the oil bath at 165° and the misc. was dried, as above, yielding 42 g. $(\text{EtO}_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Et})_2$, b.p. 132-4°, n_D²⁰ 1.4390. To the suspension of 9.2 g. Na in 200 ml. xylene was added 66.2 g. VIII, followed by 80 g. $\text{MeCH}_2\text{BrCO}_2\text{Et}$, the misc. refluxed 3 hrs. at 60°, the ppt. filtered off, and the reaction product worked up as above, yielding 65 g. $(\text{EtO}_2\text{P}(\text{O})\text{CHMeCO}_2\text{Et}$, b.p. 150-1°, n_D²⁰ 1.4292, XII (88.4 g.) and 40 g. $\text{CH}_2=\text{CN}$ were refluxed 4 hrs. in the oil bath at 165-70°.

and the mixt. was distd. as above, yielding 71 g. II, b.p.
124-5°, n_D²⁰ 1.4370. VI (15.9 g.) was added (stirring,
CaCl₂ tube) to a mixt. of 100 ml. C₆H₆, 0.09 g. Na, and 67.3
g. X kept at 25° (ice-water cooling), the mixt. heated 3 hrs.,
at 65°, cooled, neutralized with ACOH, washed with water,
NaHCO₃ soln., and again water, dried over Na₂SO₄, the
solvent removed, and the residue distd. in vacuo (pro-
cedure A), yielding the following fractions: Unchanged
X (18 g.), b.p. 74-90°, (EtO)₂P(O)CH(CH₂CH₂CN)CO₂Bt
(35 g., b.p. 100-20°, 33 g. after redist., d₄²⁰ 1.12-1.7,
n_D²⁰ 1.4470, d₄²⁰ 1.1168), and (EtO)₂P(O)CH(CH₂CH₂CN)-
CO₂Bt (XIII) (19 g.), b.p. 118-90°. X (67.3 g.) was
added (stirring, CaCl₂ tube) to 100 ml. dry C₆H₆ and 2.5
g. K (highly exothermic reaction), the mixt. cooled to room
temp., and to it was added 31.8 g. VII at 45-50° (ice-water
cooling); the mixt. then heated 3 hrs. at 60°, left 12 hrs. at
room temp., and worked up as in A, yielding 68 g. XIII
(procedure B), b.p. 145-7°, n_D²⁰ 1.4030, d₄²⁰ 1.1451. X
(50% excess) treated with VII by procedure A, yielding 57%
(EtO)₂P(O)CH(CH₂CH₂CO₂Me)CO₂Bt, b.p. 90°,
n_D²⁰ 1.4448, d₄²⁰ 1.1463. (EtO)₂P(O)CH(CH₂CH₂CO₂Me)CO₂Bt
was prep'd. in 67% yield by procedure B, using 25% excess
VII, b.p. 125-9°, n_D²⁰ 1.4568, d₄²⁰ 1.1684. (EtO)₂P(O)CH-
(CH₂CO₂Et)CO₂Bt (XIV) was prep'd. in 66% yield.

from $\text{C}_1\text{H}_3\text{Me}(\text{CHCO}_2\text{Et})$, a stoichiometric amt. of K, and 20% excess X, using procedure A (negligible heat effect), b_{25}^{25} 93°, n_D^{25} 1.4468, d₄ 1.1082. $(\text{EtO}_2\text{P(O)})\text{CH}(\text{CHPi}-\text{CH}_2\text{CO}_2\text{Et})\text{CO}_2\text{Et}$ was prep'd. in 90% yield from X and V under the same conditions as XIV; b_{25}^{25} 133°, n_D^{25} 1.4578, d₄ 1.1297. $(\text{EtO}_2\text{P(O)})\text{CBu}(\text{CH}_2\text{CH}_2\text{CN})\text{CO}_2\text{Et}$ (XV) was prep'd. in 73% yield from XI and VI (procedure A), using 0.1 mol. K per mol. of XI, b_{25}^{25} 116-18°, n_D^{25} 1.4612, d₄ 1.0631. $(\text{EtO}_2\text{P(O)})\text{CBu}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})\text{CO}_2\text{Et}$ was prep'd. in 73% yield from XI and VII, using procedure analogous to XV, b_{25}^{25} 117-19°, n_D^{25} 1.4526, d₄ 1.0973. $(\text{EtO}_2\text{P(O)}(\text{CH}_2\text{CH}_2\text{CN}))\text{CN}$ was prep'd. from II and VI (procedure B). The crude product after the removal of the solvent was crystd. from CCl_4 and ether, yield 80%; colorless needles, m. 73.5-4°, easily sol. in C_6H_6 , alc., difficulty in water, and petr. ether.

Adams Sporayfield

MICHALSKI, JER
POL.

Organophosphorus compounds of sulfur and tellurium.
Synthesis of tertiobutyltellurophosphate. Jan
Michalski and Jan Wiczorekawski (Higher Polytech. School
(Gdansk, Poland). Roczniki Chem. 28, 223-233 (1954) (English
summary); cf. C.A. 49, 3782a. Tetraethyltelluropho-
phate, $\text{Se}(\text{PO}(\text{OEt})_3)_4$ (I), was prep'd. by adding with
good stirring 0.1 mole diethyl chloro phosphate (C.A. 49, II,
Zakie) to 0.1 mole of dried anal. pure (Eti) $\text{PO}(\text{OEt})_3\text{SeNa}$ (cf.
Proc. C.A. 42, 2537c) in 100 ml. boiling anhyd. ether (Hg-
sealed stirrer, drying tube). The mixt. was refluxed 90
min., dil'l. with 60 ml. Cells in a separatory funnel, washed
with 60 ml. water, the top layer washed with 5% NaHCO_3
(about 50 ml.), H_2O , and dried over NaSO_4 . Reaction
products were distd. *in vacuo* after removing the solvent in
vacuo. The following esters were prep'd. [alcyds, % yield
b.p. (unrecd.), $\lambda_{\text{D}}^{\text{25}}$, n_{D}^{20} , and δ given]: tetra-Et (II), 68, b.p.
107°, 1.448, 1.4518, 1.2403; tetra-Pr, 79, b.p. 106-7°,
1.470, 1.4542, 1.2065; tetra-isop-Pr, 45, b.p. 93°, 1.4510,
1.4490, 1.1970; tetra-Bu, 60, b.p. 121° (with partial de-
compn.), 1.4509, 1.4540, 1.1995; di-Et di-Pr (from CIPO-
(Orth) and (PrO)₂PO(SeNa), 80, b.p. 111-12°, 1.4482,
1.448, 1.2060. Prepn. of the tetra-Me ester was unsuc-
cessful. I possess unpleasant odors, decomp. above 150°,
are sparingly sol. in H_2O and easily sol. in organic solvents,
and are less susceptible to hydrolysis than the corresponding
 O -deriva. I with concd. H_2SO_4 ppts. Se; they react with
 AgNO_3 and HgCl_2 . The proposed structure requires further
confirmation. II exhibits anticholinesterase activity.
Adam Szczyński

MICHAELSKI, J.F.N.

✓ Thionicotinic acid and dinitrophenyl derivative. [partial]
~~CH~~ *[partial]* *Journal of the Chemical Society, Samuel Acosta Chem., 1911-1914] (English summary). - Nicotinic acid (30 g.) is added in portions to 51 g. SOCl_2 . After the initial violent reaction, the mixt. is stirred on a steam bath for 3 hrs.; the excess halide is dried off, and the residue, b. 153-5° (reduced pressure), is mixed with 300 ml. dry $\text{C}_2\text{H}_5\text{N}_2$, and H_2 passed through the stirred soln. at 0-5° for 7 hrs. The mixt. is filtered; the filtrate is evapd. to dryness, powdered, washed with Et_2O , MeOH , ice- H_2O , and again with Et_2O and MeOH . Recrystn. of the powder from MeOH yields 20.5 g. thionicotinic acid, m. 145-7°, which is oxidized with iodine to the disulfide, m. 88-9°.* Chester Place

"APPROVED FOR RELEASE: 03/13/2001

CIA-RDP86-00513R001033810018-6

LESTER JONES, JR.; MURRAY C. COHEN; JAMES R. HARRIS

"Aminoalkyl Nitroxides. II.", U.S. 3,170,830, assigned to the Goodyear Tire & Rubber Company, June 1954, inventors, Lester Jones, Murray Cohen, James R. Harris.

"Aminoalkyl Nitroxides. III.", U.S. 3,170,831, assigned to the Goodyear Tire & Rubber Company, March 1955, inventors, Lester Jones, Murray Cohen, James R. Harris.

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CIA-RDP86-00513R001033810018-6"

*MICHALESKY, J.**CZ B CH*

✓ Same additional 4,4'-bis(aminomethyl)-2,2'-bikazole
L. Michaleksky and L. Borovcová (Tatra Inst. of Chem. Tech., Bratislava, Czechoslovakia) 1972-3 (1974); ref. C.A. 80: 9327g. Condensation of $\alpha\text{-C}_6\text{H}_4(\text{CO})_2\text{NCHMeCOCH}_2\text{H}_2$ (I) and $\alpha\text{-C}_6\text{H}_4(\text{CO})_2\text{NCHMeCH}_2\text{COCH}_2\text{Br}$ (II) with $(\text{CSNH}_2)_2$ gave the corresponding 4,4'-bis(2-alkylimidooethyl)-2,2'-bikazole (III), and 4,4'-bis(2-alkylimidopropyl)-2,2'-bikazole (IV), hydrolyzed to the di-HCl salt of 4,4'-bis(2-aminomethyl)-2,2'-bikazole (V) and 4,4'-bis(2-aminopropyl)-2,2'-bikazole (VI). Treating 4.6 g. $\alpha\text{-C}_6\text{H}_4(\text{CO})_2\text{NCHMeCOCH}_2\text{H}_2$ in 16 ml. AcOH with 40% HBr to decoloration, and dil. the soln. with 600 ml. ice water gave 4.6 g. I, m. 107° (from EtOH). Heating 2 g. I with 200 ml. EtOH and 400 mg. $(\text{CSNH}_2)_2$ 30 min. at 100° gave 1 g. III, m. 302-3° (from CaH_2). Refluxing 400 mg. III in 300 ml. AcOH and 20 ml. concd. HCl 8 hrs., adding 20 ml. AcOEt and 80 ml. HCl, refluxing the mixt. 16 hrs., evapg. in vacuo, removing the phthalic acid, evapg. the soln. to dryness, dissolving the residue in EtOH, and pptg. with Et₂O gave 170 mg. V, decomp. without melting above 210° (from EtOH-Et₂O); diperiodate, decomp. without m. above 210°. Similarly were prep'd. IV (69%), m. 238-8° (from EtOH), and VI (63%), decomp., without melting above 265° (diperiodate, m. 286-8° (decomp.) (from H_2O). M. Hudlicky

1016-HA-2000-11-10-01

Reaction of free thionitrogen with dialkyl phosphites
[J. Michalski and Jan Wieruszowski (Inst. Technol.
Gdansk, Poland), Rocznik Chem. 49, 127 (1975) (English
summary).] The reaction between free thionitrogen and
dialkyl phosphites is suggested to be $(RO)_2POI + [SCN]$
 $\rightarrow [RO_2PO(CNS)](I) + HSCN$. Two possible struc-
tures involving the $N:C=S$ (A) and $SC:N$ (B) for I are
considered. The observed $M.R.$ is in better accord with
A than with react with I to give dialkyl phosphorimidates.
Morris Eisenberg

6

Action of hydrogen sulfide on chloroanhydrides of organic acids of tri- and quaternary phosphorus. Synthesis of new types of anhydrides of organic acids of phosphorus. New method of synthesis of dialkyl thiophosphites and their analogs. Jan Michalski (Inst. Technol., Lodz, Poland). Recipient: [unclear] (Received 1955) (English summary).—Org. derivs. of the structure $ABPOCl$ (I) with H_2S in the presence of a tertiary amine give two derivs. of the type $[ABP(O)S]_2$. I ($A = B = MeN$) gave 16% of a compd., b.p. 91°, n_D²⁰ 1.4675, d₄²⁰ 1.1443. I ($A = Et$, and $B = EIO, PO, BuO, Et_2$, and H_2S yielded the following products, resp. % yield, b.p./mm., n_D²⁰ and d₄²⁰ given): Et₂, 120°/0.8, 1.4052, 1.1478; Et, 94, 128°/0.6, 1.4630, 1.0966; Et, 97°/0.04, 1.4000, 1.0681; Et, 140°/0.5, 1.4050, 1.1127; Et, 184-6°/0.7, 1.4922. At present the alternative $[ABP(S)(O)P(O)AB]$ structure can not be excluded. Phosphites $ABPOCl$ react with H_2S in the presence of tertiary amines to give thiophosphites of the type $ABP(SH)_2$. Examples included the following ($A = B$, % yield, b.p./mm., n_D²⁰ d₄²⁰ given): EIO_2 , 72°/15, 1.4630, 1.0765; BuO_2 , 95, 122°/18, 1.4028. —; and $A = Et$, $B = BuO$, 50, 107-8°/15, 1.4240, 0.9930.

P. Durstam

*Michałski, Van*10
02

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M-A-YOUTZ

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✓ Alkyl- and alkenylpyridines. I. Synthesis of pyridylsulfone and piperidyl sulfone by way of addition of sulfonic acids and mercaptans to 2-vinylpyridine. Osmian Achmatowicz, Elżbieta Maruszewska-Wirzunkowska, and Jan Michałski (Politech., Lublin, Poland). Roczniki Chem. 29, 7029-30 (1955) (English summary). For chemotherapeutic investigations, 2-RSO₂CH₂CH₂C₆H₅N (I) were prep'd. in the following ways: (A) To 0.05 mole 2-vinylpyridine (II) in 10 ml. alc. was added 0.06 mole of the sulfonic acid (III); the I pptd., after several min. (B) (For aliphatic III) an acidic (HCl or AcOH) soln. of the Na or Mg salt of III was extd. with Et₂O, the Et₂O distd., and the crude III dissolved in C₆H₆; to this soln. (contg. 0.1 mole III), was added 0.05 mole II and the C₆H₆ was distd. (C) To 0.25 mole RSH in 50 ml. C₆H₆ was added 0.3 mole II; the mixt. refluxed 5 hrs., and the sulfide (IV) distd. *in vacuo* and taken up in 50% AcOH and oxidized with KMnO₄ or in glacial AcOH and oxidized with 25% H₂O₂ (about 100% excess). Addn. of salts of III in presence of NaH₂PO₄ and reaction of 2-picoline with CH₃O and RSH gave poor yields. The following I were prep'd. [R, m.p. recrystn. solvent, % yield, and the method (acid used in B and oxidant in C, given parenthetically) reported]: *EI*, 62-3°, cyclohexane, 74, *B* (AcOH), 90, *B* (HCl) [HCl salt (V), m. 128-9° (from AcOEt)]; PhCH₃, 114°, xylene, 93, *A*, 94, *C* (KMnO₄), 91, *C* (H₂O₂) [V, m. 184-6° (decompn.) (from C₆H₆-alc.); *p*-MeC₆H₄, 81.5°, ligoine, 86, *A*, [V, m. 182-3° (decompn.) (from MeOH)]; *p*-AcNH₂C₆H₄ (VI), 171-2°, alc.-H₂O, 97, [from MeOH]].

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Achmatowicz, Osman

*A: p-H₂NC₆H₄, 114°, C₆H₆, 98 by hydrolysis (HCl) of VI
IV, m. 184° (decompn.) (from alc.). I treated with base
gave II and salts of III. I (or their V) reduced over PtO₂/
CH₂N(R, m.p., recryst. solvent, and % yield given):*
*Et, 37-4°, n-hexane, 98 [IV, m. 265-6° (decompn.) (from
MeOH-C₆H₆)]; PhCH₃, 85°, ligroine, 77 [IV, m. 241-6°
(decompn.) (from iso-PrOEt); HOAc salt, m. 125-6° (from
cyclohexane)]; Ph, —, 72 [IV, m. 205-6° (decompn.)
(from Me₂CO), 72% yield]; p-MeC₆H₄, 64-5°, ligroine, 92
[V, m. 200-7° (decompn.) (from MeOH-C₆H₆); N-Bz
deriv., m. 143-4° (from ligroine-C₆H₆)]; p-AcNH₂C₆H₄, —,
— [HOAc salt, m. 190-1° (from Me₂CO), 75% yield];
p-H₂NC₆H₄, 150°, toluene, 98, 2-[2-(Phenylmercapto)-
ethyl]pyridine bu 197-8°, b, 64°, n_D²⁵ 1.6066, d₄ 1.1169,
96% yield; picrate, m. 119° (decompn.) (from alc.).*

A. Semenov

PM
12

MICHALSKI, JAN

4532

Synthesis of 2,6-disubstituted and 2-methyl-4-vinyl-

Author: Jan Michałski and Kazimierz Stępniewski
Journal: Chemia 1968, 22, 1968; *J. C. S.* 1969; 1969.
2,6-Bis(2-hydroxyethyl)pyridine (I), b.p. 125-6°
and 2-methyl-4-(2-hydroxyethyl)pyridine (II), b.p. 126-7°,
were prep'd. by condensation of 2,6-butidine with CHO .
I and II gave, resp., by dehydration in presence of KOH
2,6-dienylpyridine (III), b.p. 88-9°, n_D²⁰ 1.5710 [picrate, m.
140.5° (from dil. alc.)], and 2-methyl-6-vinylpyridine
(IV), b.p. 73°, n_D²⁰ 1.5320 [picrate, m. 160.5° (from
dil. alc.)]. The following 2,6-bis(2-substituted-ethyl)-
pyridines were prep'd. from III (substitution, b.p./mm. and
m.p. picrate given): $\text{PhCH}_2\text{SO}_3^-$ — (m. 66), —; PhS_2 ,
140-51°/780, 87-8°; EtO_2N^+ , 116°/0.5, 154-5°; Rt_2N , 125-
8°/18, 63-3°; morpholine, 116°/0.5, 136-7°. From IV
were prep'd. similar compds.: PhSO_3^- — (m. 130°), 172-
3°; BuS_2 , 107-8°/0.5, 81-4°; morpholine, — (m. 120-7°),
161-5° (dipicrate). A. Semenov

M. A. V. J. T. 2

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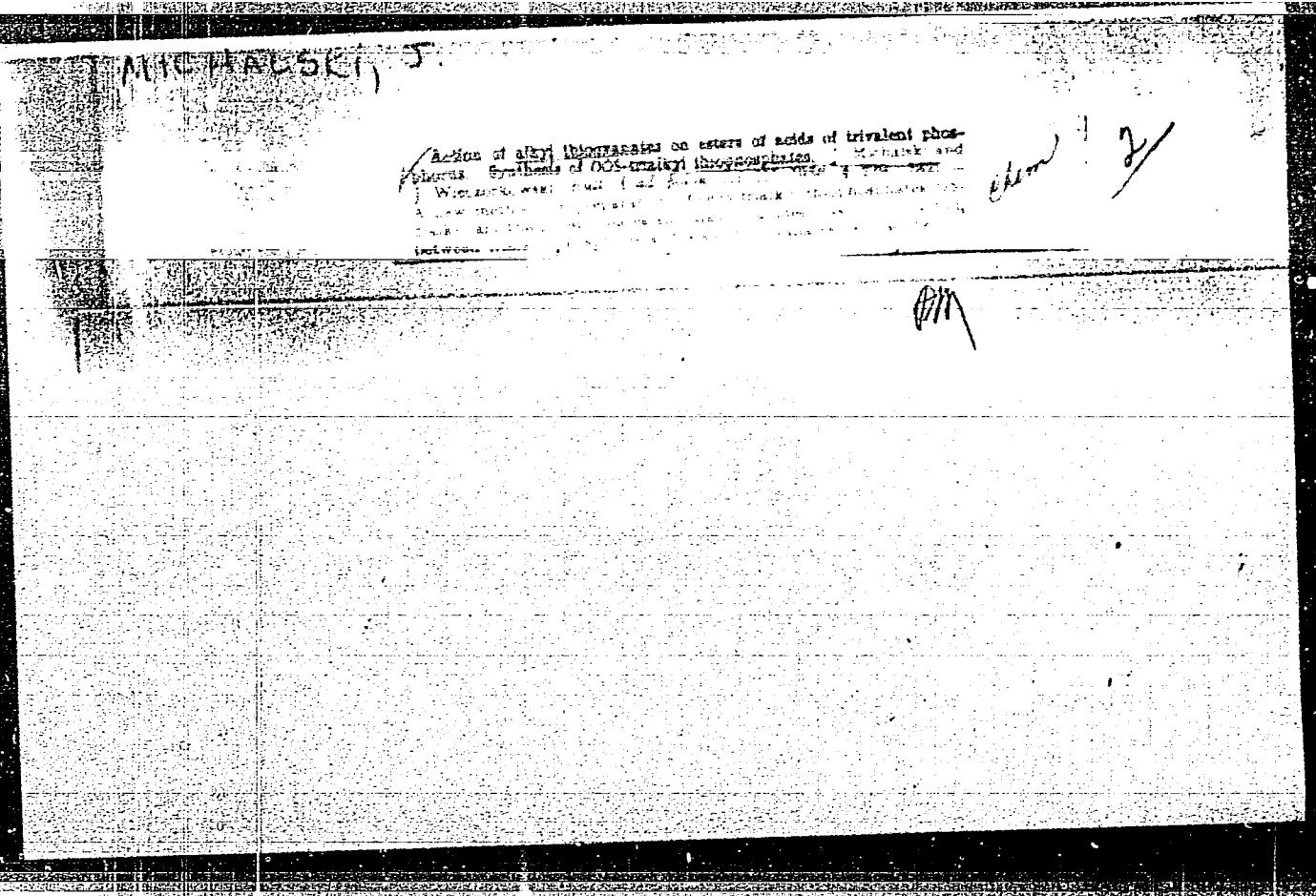
RM

MICHAVSKY

Chem. ✓ The action of alkyl thioglycates on esters of acids of trivalent phosphorus. Synthesis of O,O-trialkyl thiophosphates [M. N. K. and I. V. Arbusov]. Khim. i Tekhnol., Lekarstv. Dostav. i Prod., no. 1, Class 3, 4274-82(1956). A new method for the preparation of O,O,S-trialkyl thiophosphates, O,S-dialkyl arylthiophosphates and alkyl cyanides is described. The reaction products are not similar to those of the corresponding reaction with alkyl halides (Arbusov reaction). Tri-Et phosphite (I) and EtSCN (II) are heated in equimolar proportions in an oil bath to about 100°. After the vigorous exothermic reaction is complete, the EtCN is distd. on raising the temp. slowly to about 100-80°. Products are 91% O,O,S-tri-Et thiophosphate, b.p. 120°, n_D^{20} 1.4560, d₄₀ 1.1001, and 90% EtCN (III), b. 90°, n_D^{20} 1.3050. The following products are obtained similarly. O,O'-di-Et S-Bu thiophosphate, 90%, b. 437°, n_D^{20} 1.4580, d₄₀ 1.0618, and III, 80%, b. 96°, n_D^{20} 1.3658, are obtained from I and BuSCN. O,O'-di-Et S-Benzyl thiophosphate, 81%, b. 133-4°, n_D^{20} 1.5252, d₄₀ 1.1540, and III, 80%, b. 96°, n_D^{20} 1.3661, are obtained from I and PhCH₂SCN. O,O'-di-Bu S-Et thiophosphate, 87%, b.p. 152-3°, n_D^{20} 1.4518, d₄₀ 1.0201, and BuCN, 78% b. 139°, n_D^{20} 1.4040, are obtained from tri-Bu phosphite and II. O,S-Di-Et phenylthiophosphonate, 83%, b.p. 106-7°, n_D^{20} 1.5410, d₄₀ 1.1393, and III, 73%, b. 96°, n_D^{20} 1.3632, are obtained from di-Et phenylthiophosphonite and II. E. R. B.
PM *mk*

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CIA-RDP86-00513R001033810018-6

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CIA-RDP86-00513R001033810018-6"

MICHALSKI, T.

Sulfonic acids. I. Addition of sulfonic acid salts to α,β -unsaturated ester compounds. Synthesis of esters. O. Achmatowicz and J. Michalak [Inst. Technol., Lodz, Poland]. Roczniki Chem. 30, 212-51 (1956) (English summary).—Addn. of sulfonic acids (I), to a α,β -unsatd. compds (esters, ketones, amides, nitriles) (II) gives sulfonates. The reaction is conducted in aq. soln. in the presence of NaH₂PO₄ (0.11 mole per 0.1 mole Na salt of I and 0.12 mole II in 200 ml. water) or of CO₂, or, in the case of free acids, in aq.-alc. water, with the use of a large excess of II. The following sulfonates were prep'd. (mp. and % yield are listed): PhSO₃CH₂CH₂CO₂Me, 73-4°, 80%; α -MeC₆H₅SO₃CH₂CH₂CO₂Me, 73.5-75°, 84%; α -AcNH₂C₆H₅SO₃CH₂CH₂CO₂Me, 80.1°, 88%; Bis(C₆H₅SO₃)₂CH₂CO₂Me, 43-4.5°, 30%; Ph₂SO₃CH₂CH₂CO₂Et, (oil); CH₂CO₂Me, 42-4.5°, 30%; Ph₂SO₃CH₂CH₂CO₂Et, (oil); α -AcNH₂CH₂CH₂CO₂Et, 42-3°, 91%; α -AcNH₂CH₂CH₂CO₂Et, 125-9°, 80%; α -AcNH₂CH₂CH₂CO₂Et, 114-6°, 80%; α -AcNH₂CH₂SO₃CH₂CH₂CO₂Me, 123-4°, 45%; MeC₆H₅SO₃CH₂CH₂CH₂CO₂Me, 84-7°, 60%; PhSO₃CH₂CH₂CH₂CONH₂, 120-7°, 88%; α -AcNH₂H₂SO₄CH₂CH₂CONH₂, 110-11°, 78%; Ph₂SO₃CH₂CH₂CN, 90-4°; H₂SO₄CH₂CH₂CONH₂, 116-18°, 84%; α -MeC₆H₅SO₃(O)CHMeCH₂CN, 123-4°, 43%; α -MeC₆H₅SO₃(O)CH₂CH₂CN, 147-8.5°, 23%; α -AcNH₂CH₂CH₂CO₂Et, 133-8°, 94%; α -AcNH₂CH₂SO₃CH₂CH₂Bz, 173-80°.

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ACHMATOWICZ, O. AND MICHALSKI ...

61; $p\text{-MeC}_6\text{H}_4\text{S(O)}\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, 146-50°, 10; $\text{PhS(O)}_2\text{CH}_2\text{CH}(\text{SO}_2\text{Me})_2$, 172-3°, 85; $p\text{-MeC}_6\text{H}_4\text{S(O)}\text{CH}_2\text{CH}_2\text{SO}_2\text{Me}$, 90, M_p , 171-1°, 98; $p\text{-AcNHCH}_2\text{S(O)}\text{CH}_2\text{CH}_2\text{SO}_2\text{Me}$, 208-9°, 82; $p\text{-C}_6\text{H}_4\text{S(O)}\text{CH}_2\text{CH}_2\text{SO}_2\text{Ac}$, 201-3°, 70; $\text{EtS(O)}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{Me}$, 120-4°, 60. Some substituted sulfones were hydrolyzed with 20% HCl to give compds. listed below (m.p. and % yield are given): $\text{PhS(O)}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, 125-6°, 85; $p\text{-MeC}_6\text{H}_4\text{S(O)}\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, 112-13°, 62; $p\text{-H}_2\text{NC}_6\text{H}_4\text{S(O)}\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, 163-5°, 55; $\text{EtS(O)}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, 116-16°, 98; $\beta\text{-C}_6\text{H}_5\text{S(O)}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, 134.5-38°, 90; $\text{PhCH}_2\text{S(O)}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, 170-8.6°, 92; $p\text{-MeC}_6\text{H}_4\text{S(O)}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, 133.5-34°, 95; $p\text{-MeC}_6\text{H}_4\text{S(O)}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, 118-10°, 93; $p\text{-H}_2\text{NC}_6\text{H}_4\text{S(O)}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, 214-15°, 87.

R. Dvorko

2/2

POLAND/Optics - Spectroscopy

K-7

Abs Jour : Ref Zhur - Fizika, No 2, 1959, No 4464

Author : Michalski J., Mierzecki R., Rurarz E.
Inst : -

Title : Raman Spectra of Tetraethyl Thiopyrophosphate, Triethyl Phosphate and Triethyl Thiophosphate

Orig Pub : Roczn. chem., 1956, 30, No 2, 651-653

Abstract : Raman spectra were plotted of tetraethyl thiopyrophosphate (I), triethyl phosphate (II), triethyl thionophosphate (III) and triethyl thiophosphate (IV) and the resultant spectra were compared. The Raman spectra of I exhibit substantial differences from the spectrum of IV, but in many features it is similar to the spectra of II and III. These facts suggest that the most probable structure of the tetra alkyl thiopyrophosphates (prepared by the action H₂S on dialkyl phosphor chlorides (V) in the presence of tertiary base or condensation of V with salts of dialkyl thio phosphoric acid) can be expressed by the following formula:

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122

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APPROVED FOR RELEASE: 03/13/2001

CIA-RDP86-00513R001033810018-6"

MARUSZLWSKA-WIJCZCEROWSKA, E.; MICHALSKI, J.; SKOWRONSKA, A.

"Organophosphorous compounds with an active methylene group. II. Dialkyl 2-pyridylmethylphosphonates $(RO)_2P(O)CH_2(2-C_5H_4N)$ and dialkyl 2-pyridylmethylthiophosphonates $(RO)_2P(S)CH_2(2-C_5H_4N)$."

p. 1197 (Roczniki Chemii) Vol. 30, no. 4, 1956
Warsaw, Poland

SO: Monthly Index of East European Accessions (EAI), LC, Vol. 7, no. 4,
April 1956

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CIA-RDP86-00513R001033810018-6"

MICHALSKI, I.

✓ Action of hydrogen sulfide on dialkyl chlorophosphites. I.
Michalski and C. Kowalecki (Inst. Tech., "Politechn.",
Lodz, Poland). *Chem. & Ind. (London)* 1957, 1323-4
cf. *C.A.* 50, 10341A.—In the presence of pyridine, $(EtO)_2PCl$ (I)
(I) with 0.5 mole H_2S gives $(EtO)_2PHS$ (II) without formation
of $[(EtO)_2P]_2S$ (III), but in the presence of a strongen
base such as Et_4N , I gives III as well as II. I with II in the
presence of Et_4N gives III in good yield, but no III can be
isolated from the mixt. in the presence of excess H_2S , since
III reacts with H_2S to give II. III, b.p. 86-87°, reacts
vigorously with H_2O to give $(EtO)_2POH$ and $(EtO)_2PSH$, is
oxidized in air to $[(EtO)_2P(O)]_2S$, b.p. 86-87°, and leads to
amide formation when added to a primary amine and car-
boxylic acid mixt. R. H. Loewenstein //

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POLAND/Organic Chemistry. Synthetic Organic Chemistry.

Abstr Jour: Ref Zhur-Khim., No 13, 1958, 43439.

Author : Michalski J., Wieczorkowski J.

Inst : Polish Academy of Sciences.

Title : The Action of Free Thiocyanogen, Diacyl Disulfides,
Dialkoxyphosphinyl Disulfides on Esters of
Acids of Trivalent Phosphorus.

Craig Pub: Bull. Acad. polon. sci., 1957, cl. 3, 5, No 9, 917-921.

Abstract: Investigation of the reactions of $(C_2H_5)_3P$ (I),
 $(C_4H_9)_3P$ (II), $(C_6H_5)_3P$ (III) and $C_6H_5P(OC_2H_5)_2$
(IV) with $(SCN)_2$ (V), $(CH_3CO)_2$ (VI), $(C_2H_5)_2P(S)_2$
 $P(7)S_2$ (VII) and $C_4H_9SSP(7)(OC_2H_5)_2$ (VIII).
Listing initial substances, reaction products,
yield in %, DP in °C/m. (in parentheses temperature
in °C): I and V, $(C_2H_5)_3PS$ (IX), 62, 93.5/13.

Card : 1/3

40

POLAND/Organic Chemistry. Synthetic Organic Chemistry

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Abs Jour: Ref Zhur-Khim., No 13, 1958, 43439.

1.4486 (20); II and V, $(C_4H_9O)_3PS$, 42, 104/0.6,
156-157/11, 1.4497 (20); I and VI, IX, 96, and
 $(CH_3CO)_3$, 97, 50/12, 61-62/20, 1.4820 (21); III
and VII, $(C_4H_9O)_3PS$, 89, 148-150/0.1, —, MP
48°, and $(C_4H_9O)_4P_2O_5S$ (X), 77, 82-84/0.04, 1.4502
(25); I and VII, X, 75, $(C_2H_5O)_4P(O)SC_2H_5$ (XI), 31,
112/11, 1.4570 (20), and IX, 37; I and VIII, C_4H_9SP
(C)(OC₂H₅)₂, 95, 131-133/11, 1.4580 (20), XI, 31;
and IX, 36; IV and VII, $C_4H_9(C_4H_9O)_3-P_2O_5S$, 81,
117-118/0.05, 112/0.03, 1.5065 (20), d₄²⁰ 1.2050;
XI, 34, IX, 37. The assumption is made of an intermediate formation of the unstable $\left[RO(R')P^+(3X)(OR)S-Y\right]$, wherein R = alkyl or aryl, R' = alkoxy, aryl or phenoxy, X = CN, CH₃CO, $(C_2H_5O)_4P(O)$, C₄H₉, Y = CN, CH₃CO, $(C_2H_5O)_2P(O)$. The complex decomposes

Card : 2/3

POLAND/Organic Chemistry. Synthetic Organic Chemistry.

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Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64546.

Author : Michalski Jan, Skowronska Aleksandra

Inst :
Title : Dialkyl Ethylpyrophosphonates C₂H₅(RO)P(0)-O-
P(0)(RO)C₂H₅

Orig Pub: Roczn. chem. 1957, 31, No 1, 301-303

Abstract: Describes the means of getting C₂H₅(RO)P(0)(OR)-
R = C₂H₅ (I), iso-C₃H₇ (II), C₄H₉ (III), by way
of hydrolyzing the corresponding C₂H₅P(0)(OR)Cl (IV)
in the presence of pyridine (V) (see RZhKhim, 1958,
8038). To 0.2 moles of (IV) (R=C₂H₅), is added drop
by drop and with stirring 0.106 moles of water and
0.206 moles of (V), at 0-2°, after 20 hours (~ 20°);
the precipitate is washed in C₆H₆ and (I) is separated

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33

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"Alkyl- and alkoxypyridines. III. Pyridine sulfones and some simple sulfur derivatives with 2-pyridylmethyl residue.

Bibicita Maruszewska-Wieczorkowska and Jan Michalski
(Politechnika, Lublin, Poland). Roczniki Chem. 31, 643-61
(1957) (English summary); cf. C.A. 50, 12046k; 51, 11347a.

The following 2-C₄H₉NCH₂Y were prep'd. from 2-pyridylmethyl chloride (I) by classic methods (Y, % yield, m.p., and m.p. picrate given): SO₂Et, 97, 105°, 183-5°; SO₂Ph, 75-60, 113°, 214-16°; SO₂C₆H₅Me-*p*, 90, 155°, 107-8°; SO₂C₆H₅NHAc-*p*, 80, 193°, 229-30°; SO₂C₆H₅NH-*p*, 100, 189°, —; SC(NH₂)NH₂·HCl, 95, 152°, —; SH, 52, — (b₆, 57-8°, n_D²⁰ 1.5768, d₄ 1.1532), 163-4; SPb, 80, — (b₆, 97-8°, n_D²⁰ 1.0228, d₄ 1.1533), 124-5°; SCN, 84, — (b₆, 77-8°, n_D²⁰ 1.5751, d₄ 1.1554), 165-7°; CSNH₂, 80, 60°, 160°.

A. Kreglewski

POLAND/Organic Chemistry. Synthetic Organic Chemistry.

C

Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64543.

Author : Michalski, Jan; Wieczorkowski, Jan

Inst :

Title : Phosphoroorganic Derivatives of Sulfur and Selenium.
V. The Action of Thiocyanogen on Dialkylphosphites
and Thiophosphites. Dialkyl Isothiocyanophosphates
and Isothiocyanophosphates.

Orig Pub: Roczn. chem. 1957, 31, No 2, 585-600.

Abstract: The action of thiocyanogen (I) on $(RO)_2POH$ (II)
or $(RO)_2PSH$ (III) produces HSCN and, with a yield of
70-80%, $(RO)_2P(Z)NCS$ (IV), where Z = O (IVa), or S (IVb).
(IVa) and (IVb) can also be derived by the action of
KCNS on $(RO)_2P(O)Cl$ or $(RO)_2P(S)Cl$. Upon hydrolysis
of (IVa), HSCN is produced, as well as $(RO)_2P(O)OH$;

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POLAND/Organic Chemistry. Synthetic Organic Chemistry.

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Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64543.

upon the reaction of (IVa) with dimethylamine, there are produced $(RO)_2P(O)N(CH_3)_2$ (V) and $(CH_3)_2NH \cdot HSCN$ (VI). Upon the reaction of (IVa) with primary amines, there is produced the thiourea $(RO)_2I(O)NHC(S)NHR'$ (VII). (VIb) hydrolyzes with more difficulty. Upon its reaction with amines, there is produced $(RO)_2P(S)NHC(S)NHR'$ (VIII). To the solution of 27.6 g (II) ($R=C_6H_5$) in 100 ml. C_6H_6 , there is gradually added at 50° a solution of 0.25 moles of (I) in C_6H_6 . Stir for an hour, then after 24 hours there can be separated (IVa) ($R=C_6H_5$) (here and later in the report, yields are given in %, and b.p. in $^{\circ}C/mm$, $N^{\circ}D$, d_{4}^{20}): 80, 64-65/0/6, 1.4791, 1.1870. Similarly derived is (IVb) where $R = C_3H_7$, 74, 72-73/0.2, 1.4751, 1.1213; (IVa) ($R = iso-C_3H_7$), 77, 63-64/0.2, 1.4690, 1.1076; (IVa) ($R = C_4H_9$) 88, 86-87/0.12, 1.4718, 1.0757. To a solution

Card : 2/5

3/

POLAND/Organic Chemistry. Synthetic Organic Chemistry.

G

Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64543.

of 0.4 moles of (I) in 500 ml C₆H₆, the gradual addition during 50 hours at 0° of a solution of 46.2 g of (III) (R = C₂H₅) in 100 ml. C₆H₆, followed by centrifuging and distilling the product, gives (IVb) (R = C₂H₅), 73, 73-74/0.6, 1.5220, 1.1906. Similarly, with (IVb) (R = C₄H₉), 72, 109/0.7, 1.5088, 1.0981. To a solution of 9.7 g. of KCNS in 150 ml. of acetone, is added 17.3 g. (C₂H₅O)P(O)Cl (IX), and from the filtrate is extracted (IVa) (R=C₂H₅), yield 56%; in the presence of acetone, yield 66%. By the same method, yields are: (IVa) (R=C₂H₅), 57%, (IVb) (R=C₂H₅) 60%, (IVb) (R=C₄H₉) 62%. From 32.5 g. (C₂H₅O)₄P(S)Cl and a solution of 14.6 g. KCSN in 200 ml of acetonitrile, there is produced (IVb) (R=C₂H₅), 68. 99-102/1.8, 1.5120, 1.1275. To a solution of 14.7 g. (IVa) (R=C₂H₅) in 50 ml C₆H₆,

Card : 3/5

POLAND/Organic Chemistry. Synthetic Organic Chemistry.

G

Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64543.

there is gradually added a solution of 7 g. dimethylamine in 150 ml C₆H₆, during 24 hours. There is liberated 4.5 g of (VI), m.p. 112°; from the filtrate can be drawn (V) (R=C₂H₅), 67, 98/21, 1.4191,-. To a solution of 17.2 g. (IX) in 50 ml C₆H₆, there is added gradually 10 g. dimethylamine in 200 ml C₆H₆ at 10-12°, yield of (V) (R=C₂H₅) 78%. To a solution of 3.9 g. (IVa) (R=C₂H₅) in 40 ml ligroin are added 2.15 g benzylamine in ligroin. The remainder, after driving off the ligroin, is dissolved in C₆H₆ and washed with 15 ml 4% HCl, 5% NaHCO₃, and water, yielded (VII) (R=C₂H₅), R' = C₆H₅CH₃ 81%, m.p. 89° (in cyclohexane). Similarly derived is (VII) (R = C₂H₅) R' = cyclohexyl, yield 75%, m.p. 85° (in cyclohexane). To a solution of 4.47 g. (IVa) (R=iso-C₃H₇) in 30 ml ligroin, there is added a solution of

Card : 4/5

32

POLAND/Organic Chemistry. Synthetic Organic Chemistry.

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Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64543.

2 g. cyclohexamine in 10 ml. ligroin, yielding (VII) ($R=iso-C_3H_7$, $R'=cyclohexyl$) 92%, m.p. 106° (in cyclohexane). To a solution of 2.11 g. (IVb) ($R=C_2H_5$) in 4 ml. ligroin, there is added 1 g benzylamine in 5 ml ligroin, yielding (VIII) ($R=C_2H_5$; $R'=C_6H_5CH_3$) 88%, m.p. 78° (in ligroin or hexane). To a solution of 3.16 g. (IVb) ($R=C_2H_5$) in 40 ml n-hexane, there is added 1.5 g. cyclohexylamine in 10 ml. n. hexane, yielding (VIII) 86%, m.p. 55° (in ligroin). For previous report, see RZhKhim, 1957, 73718.

Card : 5/5

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POLAND / Organic Chemistry. Synthetic Organic Chemistry. G

Abs Jour: Ref Zhur-Khimija, No 18, 1958, 61033.

Author : Jan Michalski, Czeslaw Krawiecki.

Inst : -

Title : Dialkylselenophosphites of $(RO)_2PSeH$.

Orig Pub: Roczn. chem., 1957, 31, No 2, 715-716.

Abstract: $(C_2H_5O)_2PSeH$ (I), boiling point 42 to 43°/0.6 to 0.7 mm, $n^{25}_D = 1.4965$, $d_4^{25} = 1.3650$, was prepared by introducing dry H_2Se into cooled solution of $(C_2H_5O)_2PCl$ and equivalent amount of tertiary amine in C_6H_6 . I reacts with SO_2Cl_2 producing $(C_2H_5O)_2P(Se)Cl$, boiling point 62°/1 mm, $n^{25}_D = 1.4974$, $d_4^{25} = 1.4411$. I adducts $CH_2=CHCN$ with

Card 1/2

POLAND/Organic Chemistry Synthetic Organic Chemistry.

3-2

Abs Jour: Ref Zhur-Khim., No 24 1958, 31722.

Author : Michalski J., Strzelecka H., Wieczorkowski J.

Inst :

Title : The Phosphororganic Compounds Containing Sulfur and Selenium. VI. Amide Esters and Amides of Isothiocyanophosphoric and Isothiocynothiophosphoric Acids.

Orig Pub: Roczn. chem., 1957, 31 No 3, 879-891

Abstract: By the reaction of KCNS on $(RO)(R'N)P(O)Cl$ (I)
(here and further aR' = CH₂, bR' = C₆H₅ /sic/),
 $(RO)(R'N)F(S)Cl$ II, $(R'N)P(O)Cl$ and $(R'N)P(O)Cl$
(S)Cl, were obtained the corresponding products by
substituting chlorine for the NCS group (III-VI).
The structure of III-VI was verified by the synthesis
of addition compounds of amines. III, especially with

Card : 1/4

41

POLAND/Organic Chemistry. Synthetic Organic Chemistry

G-2

Abs Jour: Ref Zhur-Khim, no 24, 1958, 81722

a large R, are not stable, and decompose on
 $(R'_2NPO_3)_n$ and RSCN. By the action of RCNa on
 R'_2NPOCl_4 , or by the reaction of R'_2NH with
 $ROFOCl_2$, the following I were synthesized (here and
further for describing the products are given R, yield
in %, b p. in °C./mm Hg, D₂₅): I-a, C₆H₅, 72, -,
14381, 1432; I-a, C₆H₅, 69, 82-84/1, 14408, 10926;
I-b, C₆H₅, -, 96/13, 14436 (26), -. In the same
way was obtained II-a, C₆H₅, 66, 46.5-47.5/0.4, 1.4947,
-,. To the solution of 0.14 moles of KCNS in 200 ml
of CH₂CN, 0.14 moles of I-a is added, after one hour
CH₂CN is distilled under vacuum, 100 ml of benzene
is added, from the filtrate III-a was separated,
E, H₅, 35, 59-61/0.12, 1.4930, 1.1529. In the same

Card : 2/4

PCLAND/Organic Chemistry. Synthetic Organic Chemistry

7-2

Abs Jour: Ref Zhur-Khim., No 24, 1958, 81722.

84, 125-126; $\text{[(CH_3)_2N]_2F(S)NHCSNH}_2\text{C}_6\text{H}_5$, 78, 130.
Communication V, see R Zh Khim., 1958, 64543.

Card : 4/4

Reactions of thiono esters of phosphorus with halogens and sulfonyl chloride. I. Michael and Alexandra Skowronka (Inst. Technol., Warsaw, Poland). *Trans. of Inst. (London)* 1968, 1199-1200; cf. C.A. 63, 9046b. *Reactivity of* ⁵
this acids of P contg. the >P(S)OR (I) group (R = alkyl)
react readily with Cl, Br, or SO₂Cl to give phosphinyl-
sulfenyl halides, >P(O)SX, where X = Cl. Formation of a
mesoionic complex probably is involved as an intermediate.
These reactions are useful in prepg. the I group and also as
a test to distinguish between thiono esters (I) and thiole
esters, >P(O)SR, which are known to react with Cl to give
RSCl and >P(O)Cl (Stirling, C.A. 63, 14856g). Addn. of 1
molar equiv. Cl in CCl₄ to (EtO)₂P(S)OR (II), with the
temp. kept at -5°, gave 60% (EtO)₂P(O)SCl, b.p. 49-50°,
n_D²⁰ 1.4672. Similarly was obtained 70% (EtO)₂P(O)SCI.
b.p. 73-4°, n_D²⁰ 1.4665 (SO₂Cl in C₆H₆ at 0°). II and III in
CH₂Cl₂ gave (EtO)₂P(O)SBr, unstable, which with CH₃:CH₂
gave (EtO)₂P(O)SCH₂CH₂Br, b.p. 85°, n_D²⁰ 1.4600. PhOP(

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By G. Rize

✓ Organophosphorus compounds of sulfur and selenium.
 X. Action of sulfur chloride on alkyl hydrogens alkylphosphonothioates and diaryl phosphorochloride acids. Synthesis of ρ -alkoxy- ρ -alkylsulfur phosphonothioyl chlorides. Cs. Borecki, J. Michałski and St. Misiakowicz (Techn. Univ., Lublin, Poland). J. Chem. Soc. 1955, 4081-3; cf. preceding abstr.— SO_2Cl with $\text{R}(\text{R}'\text{O})\text{PSOH}$ (I) gave $\text{RPOCOR}'\text{SCl}$ (II) or $[\text{RPO}(\text{OR}')\text{S}]_2$ (III). R_2PSOH (IV) with SO_2Cl gave R_2POCl (V) or $\text{R}_2\text{PSOPOR}'$ (VI). The nomenclature used is based on the hypothetical phosphorane PH_3 and the radical phenyl, PH_3^{\cdot} . SO_2Cl (27 g.) in 30 ml. C_6H_6 added dropwise to 30.8 g. I ($\text{R} = \text{R}' = \text{Et}$) (VII) in 100 ml. C_6H_6 at -5 to 0 ° (external cooling), the solvents and gaseous products evapd. *in vacuo*, and the residue distd. gave 70% II ($\text{R} = \text{R}' = \text{Et}$) (VIII), $b_{10} 23-4$ °, $n_D^{20} 1.4810$, $d_4 1.2312$. $\text{Bu}_2\text{EtPO}_2\text{H}$ (74.3 g.) in 150 ml. Bu_2OH contg. 11 g. Na treated slowly with 15 g. S with cooling, the filtered soln. evapd. *in vacuo*, the crude Na salt taken up in 50 ml. H_2O and titrated with 90 ml. 20% HCl, the free acid extd. 3 times with 70 ml. C_6H_6 , the ext. evapd. *in vacuo*, and the residue distd. gave 51.5 g. $\text{Bu}(\text{EtO})\text{PSOH}$ (IX), $b_{10} 78$ °, $n_D^{20} 1.4821$, $d_4 1.0053$. IX (18 g.) in 60 ml. C_6H_6 treated dropwise at -10 to -5 ° (external cooling) with 13.5 g. SO_2Cl in 40 ml. C_6H_6 , the solvent evapd., and the residue distd. *in vacuo* yielded 56% II ($\text{R} = \text{Et}$, $\text{R}' = \text{Bu}$), $b_{10} 74$ °, $n_D^{20} 1.4828$. VIII (26.4 g.) heated at 60-70°/1 mm. with pota. of S and distd. gave 18.5 g. material, redistd. *in vacuo* to give the known $\text{BuPO}(\text{EtO})\text{Cl}$, $b_{10} 35-6$ °, $n_D^{20} 1.4402$. SO_2Cl (5.15 g.) in 20 ml. C_6H_6 added dropwise to 11.76 g. VII in 60 ml. C_6H_6 at 0°, the solvent and gaseous products removed *in vacuo*, and the residue distd. gave 96% III ($\text{R} = \text{R}' = \text{Et}$) (X), $n_D^{20} 1.5061$. VIII (9.47 g.) in 100 ml. C_6H_6 added

6
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dropwise to 11.75 g. VII in 60 ml. C_6H_6 at 0°, the solvent and gaseous products removed *in vacuo*, and the residue distd. gave 96% III ($\text{R} = \text{R}' = \text{Et}$) (X), $n_D^{20} 1.5061$. VIII (9.47 g.) in 100 ml. C_6H_6 added dropwise to 7.79 g. VII in 70 ml. C_6H_6 at -5 to 0°, the solvent evapd. *in vacuo*, and the residue distd. yielded 96% X. X (16.2 g.) heated at 120°/0.06 mm. and the product distd. yielded 75% authentic $\text{EtPS}(\text{OBz})\text{OP}(\text{Et})\text{OEt}$ (XI). The structure of the anhydride XI was confirmed by comparison with compds. prepd. by the action of H_2S on alkyl alkylphosphonochlorides, $\text{RPO}(\text{OR}')\text{Cl}$ (XII), in the presence of tertiary bases according to Michałski (C.A. 50, 10041a). S (16.2 g.) added portionwise to 63.5 g. Et_2PCl in 260 ml. C_6H_6 at 18-24°, the solvent evapd., and the residue distd. yielded 89% Et_2PSCl (XIII), $b_{10} 94-5$ °, $n_D^{20} 1.5292$. XIII (45 g.) treated dropwise with 25 g. NaOH in 50 ml. H_2O at 30-40°, the soln. acidified with 20% HCl and the product added to the 3 washings of the aq. layer with 50 ml. C_6H_6 , the soln. evapd., and the residue distd. yielded 78% Et_2PSOH (XIV), $b_{10} 67-8$ °, $n_D^{20} 1.5257$; cyclotriphosphine salt m. 145-7°. SO_2Cl (14.6 g.) in 60 ml. C_6H_6 added dropwise to 15 g. XIV in 60 ml. at -6 to -2 ° with ppts. of S, the solvent evapd., and the residue distd. gave 10.2 g. V ($\text{R} = \text{Et}$) (XV), $b_{10} 90-8$ °, $n_D^{20} 1.4082$. SO_2Cl (6.5 g.) in 26 ml. C_6H_6 added dropwise to 13.4 g. XIV in 30 ml. C_6H_6 at 0°, the mixt. kept 1 hr. at room temp., the filtered soln. evapd., and the residue distd. yielded 50% VI ($\text{R} = \text{Et}$) (XVI), $b_{10} 94-5$ °, $n_D^{20} 1.5030$. XIV (8 g.) in 8 ml. C_6H_6 added dropwise to 8.1 g. XV in 7 ml. C_6H_6 at 15-20°, the HCl and solvent evapd.

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in vacuo, and the residue distd. gave 96% XVI. XVI (3.7 g.) in 10 ml. C₆H₆ treated dropwise with 2.1 g. SO₂Cl₂ in 10 ml C₆H₆ at -2 to 0°, the filtered soln. evapd., and the residue distd. gave 48% XV, b.p. 104°, n_D²⁵ 1.4068. Alc. NaOEt (3.36 g. Na in 100 ml. alc.) treated with 33 g. (PhCH₃)₂POH in 200 ml. alc., the mixt. stirred with portionwise addn. of 5.3 g. S at 30-5°, the stirring continued 2 hrs., the filtered soln. evapd. *in vacuo*, and the product crystd. (alc.) gave (PhCH₃)₂PSO₂Na, m. 232-6°. The salt (31 g.) in 200 ml. H₂O decompd. by excess HCl at 0° gave (PhCH₃)₂PS-OH (XVII), m. 190-1° (1:10 alc.-C₆H₆). XVII (6.24 g.) in 120 ml. CCl₄ at -25 to -20° treated dropwise with 2.7 g. SO₂Cl₂ in 20 ml. C₆H₆, the solvent evapd. at 0° *in vacuo* with ppts. of S, the filtered soln. hydrolyzed by addn. of a few drops of water, and the product crystd. (C₆H₆) gave authentic (PhCH₃)₂PO₂H, m. 191-3°. C. R. Addinall

G-2

POLAND / Organic Chemistry. Synthetic Organic
Chemistry.

Abs Jour: Ref Zhur-Khimiya, No 23, 1958, 77747.

Author : Maruszewska-Wierzorkowska, E. and Michalski, J.
Inst : Polish Academy of Sciences.
Title : Synthesis of Organophosphorus Compounds Containing
Pyridylalkyl Radicals and Their Structural Analogs to Dialkyl-
Phosphites and Their Structural Analogs to 2-Vinyl-

pyridine.

Orig Pub: Bull Acad Polon Sci, Ser Sci Chim Geol et Geograph,
6, No 1, 19-21 (1958) (in English).

Abstract: The addition of $R'R''P(X)H$ ($R', R'' =$ alkyl or
alkoxyl, $X = O$ or S) to 2-vinylpyridine in the
presence of C_2H_5ONa at 100° or in the absence
of C_2H_5ONa under milder conditions gives
 $2-C_5H_4NCH_2R$ (I) (R , the yield in %, bp in OC/mm,

POLAND / Organic Chemistry. Synthetic Organic Chemistry.

G-2

Abs Jour: Ref Zhur-Khimiya, No 23, 1958, 77747.

Abstract: $n^{25}D$, d_4^{25} , and the mp in $^{\circ}C$ of the picrolonate are given in that order): $P(C)(OC_2H_5)_2$, 40 (60 with C_2H_5ONa), 101/0.05, 1.4938, 1.1156, 91-92; $P(C)(OC_3H_7)_2$, 99/0.05, 1.4812, 1.0591, 134-135 (decomp); $P(C)(OC_4H_9-n)_2$, 43 (65 with C_2H_5ONa), 132-0.2, 1.4841, 1.0460, --; $P(O)(OC_2H_5)C_6H_5$, 59, 143-145/0.1, 1.5560, 1.1419, picrate mp 158-159 $^{\circ}$; $P(O)(CH_2C_6H_5)_2$, 92, --, mp 118 $^{\circ}$, -, -, -, picrate mp 158-160 $^{\circ}$; $P(S)(OC_2H_5)_2$, 58, 97/0.05, 1.5101, 1.1085 (at 30 $^{\circ}$), -. The structure of I is proved by forming the picrate

Card 2/3

37